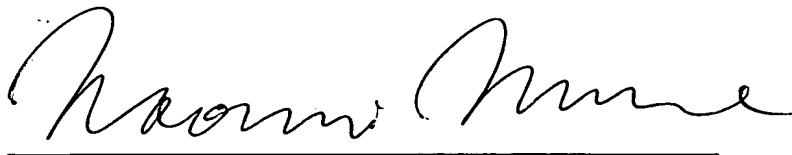# DECLARATION

I, Naomi INOUE, residing at 19-6 Mukai-machi, Gyoda-shi, Saitama, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/489,919 filed on July 25, 2003.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 27th day of December, 2004

Naomi INOUE

[Document Name]   Specification

[Title of the Invention]   Method for Producing Cerium
                           Oxide Abrasives and Cerium
                           Oxide Abrasives Obtained by the
                           Method

[Detailed Description of the Invention]

   [0001]

  [Technical Field to Which the Invention Pertains]

   The present invention relates to a method for producing

high-purity cerium oxide abrasives for planarization of

semiconductors, and to abrasives produced through the method.

   [0002]

  [Background Art]

   Conventionally, abrasives employing high-purity silicon

oxide have been used in a planarization process of

semiconductors. In recent years, high-purity cerium oxide

abrasives have been more often employed in a planarization

process. Use of cerium oxide is advantageous in that a

higher processing rate can be provided as compared with

silicon oxide abrasives and that a wide range of additives

can be used for preparing a slurry that is stable over a wide

pH range.

   [0003]

   However, cerium oxide has drawbacks, in that polished

surfaces are readily scratched as compared with

conventionally used silicon oxide abrasives and that cerium

oxide abrasives provide polishing performance less consistent

than silica-based abrasives.

[0004]

High-purity cerium oxide abrasives are produced by firing a high-purity raw material such as cerium carbonate, cerium monoxycarbonate, or cerium oxalate. Patent Document 1 discloses that cerium carbonate is employed as a raw material. Alternatively, cerium oxide abrasives are produced by synthesizing cerium hydroxide from a soluble cerium compound such as a nitrate or a chloride, firing the hydroxide, and performing pulverization and classification.

[0005]

A cerium salt of poor solubility such as cerium carbonate, cerium monoxycarbonate, or cerium oxalate is produced from a water-soluble cerium(III) salt such as a nitrate or a chloride. Elements such as alkali metals, alkaline earth metals, rare earth metals (other than cerium), and transition metal elements are removed through chemical operations such as double salt deposition, solvent extraction, and ion exchange. The purity of a poor-solubility cerium salt such as cerium carbonate depends on the purity of a soluble cerium salt employed as a raw material. At present, cerium carbonate having a metallic ion impurity content less than 100 ppm is commercially available on the market.

[0006]

One important factor affecting the polishing performance of cerium oxide abrasives is a crystal growth feature of cerium oxide. The crystal growth feature is affected by factors such as maximum firing temperature,

retention time, and temperature elevation rate. When a high firing temperature is employed, primary particles have a considerably large particle size, resulting in scratching of polished surfaces, whereas when a low firing temperature is employed, the specific surface area of cerium oxide increases, resulting in adhesion or aggregation.

[0007]

When cerium oxide abrasives are produced from cerium carbonate as a raw material, strict limitations are imposed on the aforementioned firing conditions. Since crystal morphology and purity of cerium carbonate vary in accordance with producers and product lots, optimum firing conditions are not consistently determined. Thus, the firing conditions must be modified on a case-by-case basis, and such modification causes variation in quality of cerium oxide abrasives.

A number of conventional techniques including intentionally incorporating fluorine into cerium oxide abrasives have been reported. For example, Patent Document 2 discloses a method for producing a cerium-containing abrasive characterized in that a raw material and a solution containing a fluorine component are mixed to form a slurry, whereby the raw material contained in the slurry is pulverized. The document discloses that the fluorine component concentration is preferably 0.01 wt.% to 1.0 wt.% for polishing glass substrates for electronic elements. However, the effect of fluorine described in the publication

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is to reduce coarse particles during pulverization of raw
material, and the publication provides no description of the
effect of fluorine on growth of cerium oxide particles during
firing.

Patent Document 3 discloses a cerium-containing
abrasive having a fluorine content of 0.1% or more, and a
CeO_2 content of 30% or more the entire content of rare earth
oxides. In the production of the abrasive, a rare earth
element such as Sc, Y, or La forming a stable phase composed
of Ln_2O_3 is used in an amount equal to or greater than the
amount required to form LnF_3 or LnOF, and the total amount of
the aforementioned rare earth element (as reduced to oxide)
is adjusted to 70% or less the total amount of the rare earth
metal oxides. In Patent Document 3, the relationship between
fluorine and trivalent rare earth elements is described from
the viewpoint of stoichiometry, and the effect of fluorine is
described as preventing hydration of light rare earth metal
oxide by trivalent rare earth metal fluoride or oxyfluoride.
The effect differs completely from the effect of fluorine
contained in high-purity cerium oxide having an extremely
small trivalent rare earth element content.

Patent Document 4 also describes fluoridation of light
rare earth elements. The gist of Patent Document 5 is
identical to that of Patent Document 4.

Patent Document 6 describes a method of quality
inspection of abrasives which contain a fluorine component
and La and Nd in amounts of 0.5 at.% or more based on Ce and

have a specific surface area of 12 m^2/g or less. The

publication describes the relationship between the fluorine

content and the firing temperature in the presence of a

relatively large amount of La, Nd, and fluorine, but provides

no description about characteristic growth of particles of

high-purity cerium oxide generally having an La content less

than 0.01%.

Patent Document 7 discloses an abrasive characterized

by having a ratio of cerium oxide content/total rare earth

element content of 95% or more and having a fluorine content

of 1 wt.% or less. The example section of patent Document 7

describes firing at 750°C, but describes no relationship

between optimum firing temperature and fluorine content

(microamount of 0.05% (500 ppm) or less).

The allowable metal impurity level of cerium oxide

abrasives employed for polishing semiconductors is subjected

to strict limitations, as compared with conventionally

employed cerium-containing abrasives. In order to satisfy

the impurity level, high-purity (catalyst grade) cerium

carbonate is often employed as a raw material. This means

that cerium carbonate from which fluorine has been removed or

cerium carbonate having an uncontrolled fluorine content is

employed as a raw material.

In Patent Document 8, a wide range of particle size of

cerium carbonate is claimed, along with a wide range of

firing temperature (600°C to 900°C). However, in order to

produce cerium oxide for semiconductor abrasives through

firing, firing temperature must be controlled in a narrower range. Patent Document 8 provides no description about the effect of fluorine as an impurity element under such strict quality control conditions, since the presence of fluorine does not affect high-purity cerium carbonate for conventional use.

[0008]

[Patent Document 1]

Japanese Patent Application Laid-Open (*kokai*) No. 11-181404

[Patent Document 2]

Japanese Patent Application Laid-Open (*kokai*) No. 2002-327171

[Patent Document 3]

Japanese Patent Application Laid-Open (*kokai*) No. 2003-27044

[Patent Document 4]

Japanese Patent Application Laid-Open (*kokai*) No. 9-183966

[Patent Document 5]

Japanese Patent Application Laid-Open (*kokai*) No. 2003-27044

[Patent Document 6]

Japanese Patent Application Laid-Open (*kokai*) No. 2002-97458

[Patent Document 7]

Japanese Patent Application Laid-Open (*kokai*) No. 2001-89748

[Patent Document 8]

Japanese Patent Application Laid-Open (*kokai*) No. 11-181404

[0009]

[Problems to be Solved by the Invention]

An object of the present invention is to provide a method for producing a cerium oxide abrasive from cerium

carbonate as a raw material, without variation in quality, on the basis of studies on variation in quality generated during firing of cerium carbonate.

[0010]

[Means for Solving the Problems]

The present inventor has revealed that fluorine contained in cerium carbonate affects crystal growth of cerium oxide, and has found that variation in crystal growth feature during firing can be prevented by controlling firing conditions in accordance with the fluorine content. According to the method of the present invention, abrasives without variation in quality can be produced from fluorine-containing cerium carbonate serving as a raw material.

[0011]

Accordingly, the present invention provides the following.

(1) A method for producing a cerium oxide abrasive, characterized in that the method comprises firing cerium carbonate serving as a raw material at a firing temperature T (°C) selected in accordance with the fluorine content F (ppm by mass) of the cerium carbonate, the temperature falling within a range defined by the formula:

$$730 - 14[\log(F)] \leq T \leq 790 - 10[\log(F)].$$

[0012]

(2) A cerium oxide abrasive produced through a method for producing a cerium oxide abrasive as recited in (1) above, characterized in that cerium oxide, when being suspended in

an alkali solution having a pH of nine or higher, causes elution of fluoride ions in an amount of 20 ppm by mass to 1,000 ppm by mass.

(3) A cerium oxide abrasive slurry produced through a method for producing a cerium oxide abrasive as recited in (1) above, characterized in that the cerium oxide abrasive slurry comprises cerium oxide in an amount of 0.5 mass% to 50 mass%, water, and a dispersant capable of dispersing cerium oxide, and the slurry has a fluoride ion concentration in a supernatant of 10 ppm to 500 ppm.

[0013]

(4) A method for producing a cerium oxide abrasive slurry, characterized in that the method comprises washing, with water, a cerium oxide abrasive slurry as recited in (3) above.

(5) A cerium oxide abrasive slurry produced through a method as recited in (4) above, characterized in that the slurry has a soluble fluoride concentration of 10 ppm by mass or less.

(6) A cerium oxide abrasive as described in (2) above, wherein the abrasive has an insoluble fluorine content of 1 to 100 ppm by mass based on cerium oxide.

[0014]

(7) A cerium oxide abrasive produced through a method as recited in (1) above from cerium carbonate having a fluorine content of 10 to 500 ppm serving as a raw material, wherein the abrasive has a specific surface area of 9.5 to

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12.2 m^2/g.

[0015]

[Modes for Carrying Out the Invention]

The present invention is directed to a method for producing a cerium oxide abrasive including firing cerium carbonate. The present inventor has found that a small amount of fluorine contained in cerium carbonate affects a crystallization feature of cerium oxide formed through firing, and that variation in crystallization feature can be prevented by controlling firing temperature in accordance with the fluorine content.

[0016]

Conventionally, low-quality cerium oxide abrasives, which may contain fluorine, are produced from cerium carbonate containing a large amount of fluorine serving as a raw material, whereas high-quality cerium oxide abrasives, which preferably contain no fluorine, are produced from high-purity cerium carbonate from which a fluorine impurity has been removed. When a raw material contains a trace amount of fluorine, such a raw material is considered pure cerium carbonate while the presence of fluorine is ignored, and is fired at an optimum firing temperature of pure cerium carbonate. As a result, variations arise in quality of the produced cerium oxide abrasives. The present inventor focused on the impurity present in a small amount in cerium carbonate, and has found that the amount of fluorine contained in cerium carbonate serving as a raw material

determines the quality of fired cerium oxide. The present inventor has also found the following phenomena. When high-purity cerium carbonate having a fluorine content less than 5 ppm by mass is fired, the produced cerium oxide has satisfactory crystal quality and specific surface area, whereas when the fluorine content is 10 ppm by mass or more, the fired cerium oxide undergoes excessive crystal growth and has a decreased specific surface area. The tendency of overgrowth and decrease in surface area becomes more remarkable as the fluorine content increases. The present inventor has also found that a crystallization feature and the specific surface area of cerium oxide can be precisely optimized by lowering the firing temperature with increasing fluorine content. Notably, high-purity cerium carbonate rarely has a fluorine content in excess of 500 ppm, and locally occurring anomalous particle growth of high-purity cerium oxide containing small amounts of other rare earth elements (e.g., La) is difficult to avoid by simply lowering the firing temperature. Thus, the upper limit of the fluorine content in the present invention is 500 ppm, preferably 300 ppm.

[0017]

According to the present invention, cerium carbonate serving as a raw material is fired at a lower firing temperature with increasing fluorine content of the raw material, whereby the produced cerium oxide has excellent quality (i.e., crystal quality and specific surface area)

comparable to that of cerium oxide produced from pure cerium carbonate as a raw material.

Fig. 1 shows the relationship between specific surface area and optimum firing temperature with respect to different fluorine contents of starting cerium carbonate. In Fig. 1, the specific surface area decreases as the firing temperature is elevated, regardless of fluorine content (less than 5 ppm, 60 ppm, and 300 ppm) in cerium carbonate serving as a raw material. When the fluorine content of cerium carbonate serving as a raw material increases, the specific surface area decreases. Therefore, when cerium carbonate serving as a raw material has a large fluorine content, the firing temperature is lowered in accordance with the fluorine content, thereby yielding cerium oxide having an optimum specific surface area. The preferred specific surface area of cerium oxide varies depending on use thereof and the particle size of abrasives. In the abrasive of the present invention, cerium oxide preferably has a specific surface area of 9.5 to 12.2 m^2/g, most preferably 10.5 to 11.5 m^2/g. Although not illustrated, when cerium carbonate having a high fluorine content is fired at high firing temperature, excessive growth occurs, forming scratches on the polished surface. When the specific surface area falls within the aforementioned preferred or optimum range, the crystal-related properties are preferable or most preferable.

[0018]

According to the present invention, cerium carbonate

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serving as a raw material having a fluorine content of 10 to 500 ppm, preferably 50 to 300 ppm, is fired at a temperature satisfying the equation:

T = (700 + A) - B[log(F)]

(wherein T represents firing temperature (°C), F represents fluorine content (ppm by mass), and A and B represent constants that are determined by the firing furnace and temperature elevation conditions employed), to thereby form high-quality cerium oxide suitable for abrasives, even through pure cerium carbonate serving as a raw material having a fluorine content less than 5 ppm is not employed.

[0019]

The value "A" is determined from the results of firing experiments of cerium carbonate having a fluorine content less than 10 ppm. For example, when pure cerium carbonate serving as a raw material having a fluorine content less than 5 ppm is employed, the term B[log(F)] is virtually negligible. Thus, the value "A" is obtained from the equation:
T (optimum firing temperature determined) = (700 + A).

The value "B" is obtained from the equation:
T (optimum firing temperature) = (700 + A) - B[log(F)], by inputting a predetermined "A" value and a specific fluorine content (F) [10 to 500 ppm, preferably 50 to 300 ppm] of cerium carbonate serving as a raw material.

[0020]

Generally, the value "A" is 30 to 90, and the value "B" is 10 to 14.

Accordingly, the firing temperature T generally falls within a range defined by the following formula:

730 + 14[log(F)] ≤ T ≤ 790 + 10[log(F)]. Fig. 2 shows this range.

Cerium carbonate is produced by adding a soluble carbonate salt such as ammonium hydrogencarbonate to a soluble cerium salt such as cerium nitrate or cerium chloride.

[0021]

When an aqueous cerium nitrate solution is used as a raw material, nitrate ions are generally incorporated into cerium carbonate in an amount of about 500 ppm to about 5,000 ppm. When an aqueous cerium chloride solution is used as a raw material, similarly, chloride ions are generally incorporated into cerium carbonate in an amount of 500 ppm to 5,000 ppm. These nitrate ions and chloride ions are difficult to identify through a crystallographic method such as X-ray diffraction. Even though the cerium carbonate is repeatedly washed with water, the nitrate ion content or the chloride ion content is not reduced substantially.

[0022]

Cerium carbonate serving as a raw material for cerium oxide abrasives is preferably cerium carbonate produced through deposition from cerium nitrate. More preferably, the cerium carbonate has a halogen element (other than fluorine) content or a sulfate ion content less than 10 ppm. As compared with nitrate ions, chloride ions and sulfate ions are more strongly adsorbed to cerium oxide even after firing.

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When such cerium oxide is put into water, chloride ions or sulfate ions are released from cerium oxide, and these ions may adversely affect the dispersion state.

[0023]

Generally, rare earth metal fluorides have poor solubility in water. If fluoride ions are present in an aqueous solution of a soluble cerium salt such as cerium nitrate or cerium chloride, cerium fluoride is precipitated. When an aqueous ammonium fluoride solution is added to an aqueous cerium nitrate solution, cerium fluoride is precipitated. Thus, when an aqueous soluble cerium salt solution of high purity is prepared, no fluorine is considered to remain in the solution.

[0024]

However, a rare earth metal and fluorine form a stable complex within a specific pH range, and the complex can be dissolved. Such a rare earth metal-fluorine complex is very stable, and is often applied to fluorine analysis. The La-alizarin complexon method, which employs a property of complexation by extraction of La from an La-alizarin complexon by fluorine at pH 5 to 5.3, is known as a method for fluorine analysis.

[0025]

Fluorine serves as a particle growth accelerator, and the property is well known with respect to alumina. Among rare earth metal oxide abrasives, bastnaesite-based abrasives are well known. In the production of bastnaesite-based

abrasives, fluorine contained in a raw material promotes crystal growth, thereby producing abrasives having high processing performance.

[0026]

Ores such as bastnaesite, monazite, and ion-adsorbed ores are known as rare earth ores. Among them, bastnaesite ore is a type of fluoride and serves as a fluorine source. If an appropriate chemical treatment is performed, fluorine can be removed even when bastnaesite is employed. The fluorine content of high-purity cerium carbonate varies in accordance with the method for producing high-purity cerium carbonate. By determining the fluorine content of cerium carbonate produced through purification of any ore, and by employing firing conditions suitable for the fluorine content, variation-free crystal properties can be assured.

[0027]

The fluorine content of cerium carbonate may be determined by dissolving cerium carbonate in sulfuric acid and subjecting the solution to anion chromatography. Alternatively, the fluorine content may also be determined by dissolving cerium carbonate in sulfuric acid, adding silicon oxide to the aqueous solution, subjecting the mixture to distillation at 150°C, and subjecting the distillate to anion chromatography or colorimetric analysis based on the La-alizarin complexon method.

[0028]

The soluble fluorine content of cerium oxide may be

determined by suspending cerium oxide in an aqueous alkaline solution and subjecting the supernatant to anion chromatography. Alternatively, colorimetric analysis may be employed. The total fluorine content of cerium oxide may be determined by alkali-fusing cerium oxide, followed by distillation and the aforementioned procedure. The difference between the total fluorine content and the soluble fluorine content provides the insoluble fluorine content.

[0029]

Crystallinity of cerium oxide is evaluated through a known means such as observation under a transmission electron microscope or a scanning electron microscope.

[0030]

Determination of an X-ray diffraction peak width is employed for roughly, and indirectly, evaluating the entirety of a sample. When cerium oxide is a sample, the most intense peak (111) is generally employed. However, diffraction at a higher angle is preferably employed for enhancing precision, from the viewpoint of quality control of abrasives. Strictly speaking, in order to determine a half-width, a monochrometer is not used so as to avoid influence of adjustment of the monochrometer, and the intensity ratio of $CuK\alpha1$ to $K\alpha2$ must be adjusted to 2 : 1 by use of an Ni filter, with performing peak separation based on a Cauchy-type curve or a Gaussian curve. However, routine measurement can be carried out through comparison with a standard sample.

[0031]

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Specific surface area is more readily determined, and the values are employed in production step control. Notably, X-ray diffraction analysis values and specific surface area are parameters which reflect crystallinity as well as other properties. Thus, these parameters must be determined under normalized conditions.

[0032]

The gist of the present invention resides in controlling firing temperature so as to compensate a particle growth promoting effect exerted by fluorine, and the invention has been derived from the inventor's finding that fluorine is readily incorporated into high-purity cerium carbonate, which finding was obtained through his research focusing on the role of anionic impurities, which have not been considered to be a factor of quality variation in cerium oxide abrasives produced from high-purity cerium carbonate. According to the present invention, high-purity cerium oxide abrasives can be provided from cerium carbonate containing fluorine as an impurity, without variation in quality.

[0033]

The range of modifying firing temperature in accordance with the fluorine content is about 10°C to about 50°C. Thus, in the production of cerium oxide, wherein small-scale firing test results generally do not coincide with the mass production results for a variety of reasons, a means for determining firing temperature in accordance with the fluorine content is advantageous from the viewpoint of

enhancement of production efficiency and reduction of variation in quality.

[0034]

[Examples]

The present invention will next be described in detail by way of examples, which should not be construed as limiting the invention thereto.

[0035]

Referential Example (Cerium oxide slurry production 1)

Cerium carbonate (fluorine content: <5 ppm) (1 kg) was placed in an alumina crucible and fired at 780°C for three hours, to thereby produce a cerium oxide powder. The powder (1.2 kg) was further pulverized by use of a ball mill in a dry format, and the pulverization was terminated when the cumulative amount of the pulverized product which had passed through a 1-μm sieve reached 50%, as determined by means of a laser diffraction particle size distribution analyzer (CILAS 850, product of CILAS ALCATEL). A portion of the thus-pulverized cerium oxide powder was employed as a sample for soluble fluorine analysis. The produced cerium oxide powder (600 g) was added to water (1,400 g), and a dispersant (commercial product) (3 g) was added to the mixture, followed by mixing by means of a high-speed mixer, to thereby form a slurry. The slurry was placed in a 2-L beaker and allowed to stand for 24 hours. An upper liquid portion (from the liquid surface of the slurry to the depth of 10 cm) was collected from the slurry through settling classification. The

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collected cerium oxide slurry was dried at 150°C, and the dried product was employed as a sample for specific surface area determination and a sample for X-ray diffraction analysis. Specific surface area was determined by use of Multisorb (product of Yuasa Kikai), and X-ray diffractometry was performed by use of an X-ray diffractometer (product of Rigaku Denki Kogyo) employing a high-angle diffraction ray corresponding to Miller indices of (440) so as to enhance measurement precision of half-width values. Soluble fluorine content was determined through ion chromatography, wherein the samples were prepared by adding pulverized product (1 g) of cerium oxide to a 0.01 mol/L aqueous sodium hydroxide solution, subjecting the mixture to ultrasonic dispersion for 20 minutes, and collecting the supernatant through filtration. Soluble fluorine content of the slurry was determined through ion chromatography, wherein the samples were prepared by diluting the aforementioned slurry collected through settling classification with pure water so as to adjust the slurry concentration to 10%, centrifuging the slurry, collecting the supernatant, and subjecting the supernatant to filtration.

[0036]

Example 1 (Cerium oxide slurry production 2)

In a manner similar to Referential Example, cerium carbonate (1 kg) having a fluorine content of 300 ppm was fired at 750°C for three hours, and analytical samples were prepared.

[0037]

Example 2 (Cerium oxide slurry production 3)

In a manner similar to Referential Example, cerium carbonate (1 kg) having a fluorine content of 60 ppm was fired at 760°C for three hours, and analytical samples were prepared.

[0038]

Comparative Example 1 (Cerium oxide slurry production 4)

In a manner similar to Referential Example, cerium carbonate (1 kg) having a fluorine content of 300 ppm was fired at 780°C, and analytical samples were prepared.

[0039]

Comparative Example 2 (Cerium oxide slurry production 5)

In a manner similar to Referential Example, cerium carbonate (1 kg) having a fluorine content of 60 ppm was fired at 780°C, and analytical samples were prepared.

[0040]

[Table 1]

	Fluorine concentration in cerium carbonate (ppm)	Firing temperature (°C)	Specific surface area (m^2/g)	Half-width (Å)
Ref. Ex.	<5	780	10.8	0.45
Ex. 1	300	750	10.6	0.44
Ex. 2	60	760	10.7	0.44
Comp. Ex. 1	300	780	7.8	0.33
Comp. Ex. 2	60	780	8.7	0.37

[0041]

Cerium oxide samples produced by firing cerium carbonate containing fluorine at 780°C (Comp. Exs. 1 and 2) were found to have a small specific surface area and a small

half-width, as compared with a cerium oxide sample produced by firing cerium carbonate (fluorine content <5 ppm) at the same temperature. The results indicate that the samples of Comparative Examples 1 and 2 have a larger crystallite size. Cerium oxide samples produced by firing cerium carbonate containing fluorine at a lowered temperature (Exs. 1 and 2) were found to have a specific surface area and a half-width comparable to those of the sample of Referential Example.

[0042]

[Table 2]

	Fluoride ion concentration of NaOH solution (leachant) (μg/g-ceria)	Fluoride ion concentration of 10% slurry (μm/mL-slurry)
Ref. Ex.	<5	<5
Ex. 1	230	40
Ex. 2	40	10
Comp. Ex. 1	220	38
Comp. Ex. 2	40	10

[0043]

In all the samples (in Examples 1 and 2 and Comparative Examples 1 and 2), soluble fluorine was detected. Fluorine contained in the commercial dispersant for preparing each slurry sample was also present in each supernatant in the form of fluoride ions.

[0044]

Example 3 (Production of cerium carbonate)

Cerium carbonate (fluorine content: 300 ppm) (500 g) was dissolved in nitric acid in an amount of 5% less than the stoichiometric amount. A portion of cerium carbonate

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remained undissolved. After the system had been left to stand overnight, the supernatant was collected through decantation and filtered by means of a Teflon membrane filter (0.2 μm). An aqueous ammonium hydrogencarbonate solution was added dropwise to the filtrate, to thereby re-precipitate cerium carbonate. The cerium carbonate precipitated in the course of addition of cerium carbonate was sampled several times, and each sample was washed with water and subjected to fluorine analysis. The supernatant obtained after completion of precipitation of cerium carbonate was also analyzed in terms of fluorine content. As a result, each re-precipitated cerium carbonate sample was found to have a fluorine content of about 40 to about 50 ppm, indicating that fluorine was incorporated into cerium carbonate in a constant amount from the start to the end of precipitation. The supernatant was found to have a fluorine concentration of <5 ppm. Thus, the virtually entire amount of fluorine that had been present in the aqueous cerium nitrate solution was incorporated into cerium carbonate by the end of precipitation.

[0045]

[Table 3]

	Fluorine concentration
Starting cerium carbonate	300 ppm
Precipitation 1/4	47 ppm
Precipitation 2/4	——
Precipitation 3/4	37 ppm
Precipitation 4/4	42 ppm
Supernatant	<5 ppm

[0046]

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Example 4 (Washing cerium oxide slurry with water)

A 5% slurry was prepared from cerium carbonate employed in Example 1. The slurry (30 kg) was washed with water by use of a microfilter. Fluoride ion concentration of each filtrate was determined before and after washing with water. As used herein, the "filtrate" was obtained by centrifuging a slurry and filtering the supernatant by means of a membrane filter. Fluoride ion concentration of each filtrate was determined through ion chromatography. Soluble fluorine concentration was found to have been lowered through washing.

[0047]

[Table 4]

	Fluoride ion concentration
Slurry before washing with water	40 ppm
Slurry after washing with water	2 ppm

*Fluoride ion concentration based on 10% slurry

[0048]

Example 5 (Insoluble fluorine analysis)

An alkaline flux was added to the slurry which had been washed with water in Example 4. The mixture was gradually heated, to thereby cause alkali fusion of cerium oxide. The fused product was analyzed in terms of fluorine content. The results showed that fluorine was detected in an amount of 30 ppm based on cerium oxide. A portion of fluorine species contained in cerium oxide was identified to be insoluble.

[0049]

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Example 6 (Polishing test)

Concentration of each of the slurry samples prepared in Referential Example, Examples 1 and 2, Comparative Example 1 and 2, and Example 4 was adjusted 1%. A polishing test was carried out by use of each slurry sample.

[Polishing conditions]

Workpiece to be polished:

A silicon dioxide film (thickness: approximately 1 μm) formed on a silicon wafer (6 inch φ, thickness: 625 μm) through CVD.

Pad:

Two-layer polishing Pad for semiconductor devices (IC 1000/SUBA 400, product of Rodel Nitta).

[0050]

Polishing machine:

One-side polishing machine for semiconductor devices (Model SH-24, table plate size: 610 mm; manufactured by Speedfam, Inc.)

Table rotation: 70 rpm

Working pressure: 300 gf/cm^2

Slurry feeder: 100 mL/min

Polishing time: 1 min

[0051]

[Evaluation items and methods]

Polishing rate: Film thickness measuring apparatus (optical interference method)

Defects: Dark-field microscopic observation (magnification of

×200, observation of about 3% of the surface area of the wafer, reducing the number of detected defects to count/cm^2). Remaining abrasive grains: Dark-field microscopic observation (magnification of ×200, observation of about 3% of the surface area of the wafer, reducing the number of detected defects to count/cm^2).

[0052]

Each workpiece (wafer) was subjected to the aforementioned polishing test, scrub-washing with pure water, and spin-drying, and the thus-treated wafer was evaluated.

[0053]

[Table 5]

	Polishing rate (Å/min)	Scratches by polishing (count/cm^2)	Remaining grains (count/cm^2)
Ref. Ex.	4,340	0	3.20
Ex. 1	4,300	0	3.05
Ex. 2	4,370	0	3.18
Comp. Ex. 1	5,100	8	2.58
Comp. Ex. 2	4,790	5	2.88
Ex. 4	4,410	0	3.30

[0054]

Although the slurry samples of Comparative Examples 1 and 2 provided high polishing rate, a number of scratches were formed during polishing, thereby deteriorating the quality of the polished surface. The presence of soluble fluorine had no adverse effect on the quality of the polished surface. However, deterioration of the quality of polished surfaces due to excessive crystal growth was predominant.

[0055]

[Effects of the Invention]

The abrasives produced by the method for producing abrasives of the present invention provide a consistent process rate and consistent quality of polished surfaces. Thus, the abrasives are preferably employed in a polishing composition for semiconductors.

[Brief Description of the Drawings]

[Fig. 1]

Relationship between specific surface area and optimum firing temperature with respect to different fluorine contents of starting cerium carbonate.
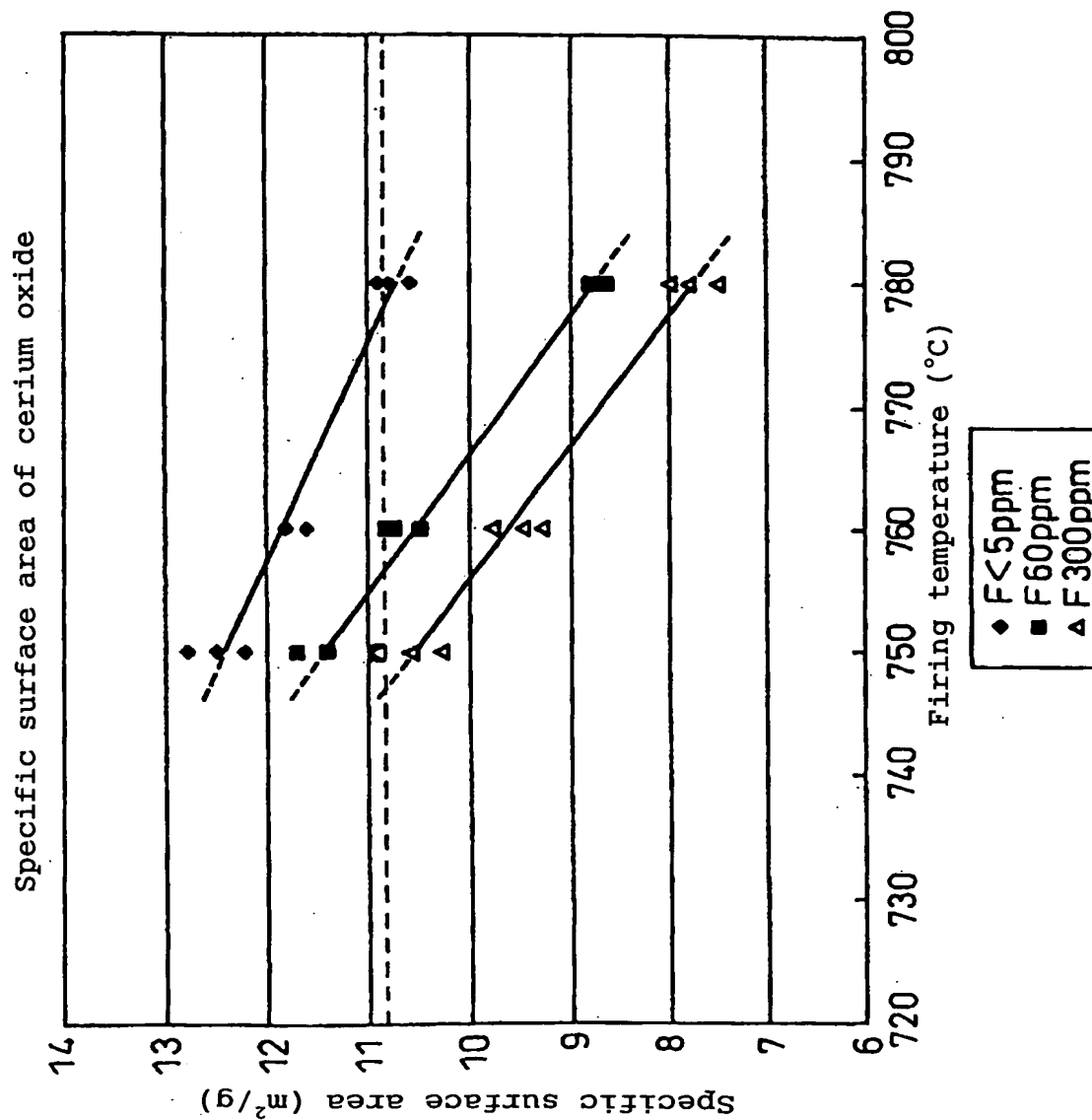
[Fig. 2]

Relationship between fluorine content of starting cerium carbonate and firing temperature range.

[Document Name]   Drawings

   [Fig. 1]

Fig. 1

Specific surface area of cerium oxide

[Fig. 2]

Fig. 2